Considerations in the Weathering of Wood-Plastic Composites

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Abstract

During weathering, wood-plastic composites (WPCs) can fade and lose stiffness and strength. Weathering variables that induce these changes include exposure to UV light and water. Each variable degrades WPCs independently, but can also act synergistically. Recent efforts have highlighted the need to understand how WPCs weather, and to develop schemes for protection. The first plan of attack is often to adapt photostabilizers currently used to protect polyolefins in WPCs. Another effective option is to improve the surface of the WPCs by changing manufacturing methods and/or conditions. This paper identifies three main factors that influence WPC weathering; photostabilization, processing conditions, and weathering variables. The effect of each factor is discussed, and an example presented in detail.

Introduction

Wood-plastic composite (WPC) lumber is promoted as a low-maintenance high-durability product [1]. However, after a decade of exterior use in the construction industry questions have resulted regarding durability. Weathering is of particular concern because it has been well documented that WPCs exposed to weathering may experience color change, which affects their aesthetic appeal, as well as mechanical property loss, which limits their performance [2-9]. Weathering exposure can include both degradation due to UV light (photodegradation) and water exposure. Recently, efforts have been focused on understanding how to mitigate changes that occur to WPCs during weathering [2-5, 7].

Photodegradation of WPCs is a difficult problem, complicated by the fact that each component may degrade via a different mechanism. Photodegradation of polyolefins originates from excited polymer–oxygen complexes [10] and is caused mainly by the introduction of catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds introduced during polymer manufacturing. Even in the absence of significant UV absorption, small amounts of these impurities can be sufficient to induce polymer degradation [11]. Degradation of polymers

as a result of photooxidation has undesirable effects, such as loss of strength, stiffness, and surface quality. Slowing down or stopping the reactions that are responsible for degradation is necessary for UV stabilization.

The individual components of wood—cellulose, hemicellulose, lignin, and extractives—are variously susceptible to photodegradation [12]. The weathering of wood is confined to the wood surface and involves photo-induced breakdown of lignin to water-soluble reaction products, which leads to the generation of chromophoric functional groups such as carbonyls, carboxylic acids, quinones, and hydroperoxy radicals [12].

Water exposure is another weathering variable that can degrade the mechanical properties of WPCs [13-18]. When WPCs are exposed to moisture, the hydrophilic wood fiber swells. This can cause local yielding of the plastic due to swelling stress, fracture of wood particles due to restrained swelling, and interfacial breakdown. Cracks formed in the plastic can also contribute to penetration of water into the composite [13,14]. Exposing WPCs to moisture results in a drop in flexural modulus of elasticity (MOE) and strength by degrading the wood–plastic interface [13-15]. The amount of moisture absorbed can be influenced by wood flour content, wood particle size, and processing method [13,16,17], as well as certain additives such as coupling agents.

Although photodegradation of both polyolefins and wood have been extensively examined, the understanding of WPC weathering continues to evolve. This paper summarizes the main effects identified that contribute to the weathering performance of WPCs. The effects of photostabilization, processing conditions, and weathering variables will be addressed.

Photostabilization

The first plan of attack to improve the weatherability of WPCs is often to add photostabilizers. Photostabilizers are compounds developed to protect polymers and combat UV degradation. They are generally classified according to the degradation mechanism they hinder. Ultraviolet absorbers (UVAs) and free radical scavengers are important photostabilizers for polyolefins. Commercial UVAs are readily available as benzophenones and benzotriazoles [11]. A relatively new class of materials, hindered amine light stabilizers (HALS), has also been extensively examined for polyolefin protection as free radical scavengers [10,11,19,20]. Pigments physically block light, thereby protecting the composite from photodegradation.

Many photostabilizers that were developed for use in unfilled polyolefins are being adapted for use in WPCs and is an active area of research [2-7]. Pigments, ultraviolet absorbers, and hindered amine light stablilizers have been used with some success in mitigating changes that occur during WPC weathering.

Pigments were shown to mitigate the increase in lightness and significantly increase the flexural property retention of WPCs after accelerated weathering [2]. Lundin [3] investigated the effect of hindered amine light stabilizer (HALS) content on the lightness and mechanical property loss of WPCs. The author reported that the addition of HALS to the composites did not affect color change caused by accelerated weathering, and slightly improved the mechanical property retention [3]. Stark et al. [4] examined the effect of a low molecular weight HALS, a high molecular weight HALS, a benzotriazole ultraviolet absorber (UVA), and a pigment on the changes in lightness and mechanical properties of WPCs after weathering. Only the UVA and pigment significantly reduced composite lightening and loss in mechanical properties. Regardless of molecular weight, HALS was found to be ineffective in protecting the composite against surface discoloration and flexural property loss. Muasher and Sain also evaluated the performance of HALS and UVAs in stabilizing the color WPCs. They found that high molecular weight diester HALS exhibited synergism with a benzotriazole UVA [5].

We employed Fourier transform infrared spectroscopy (FTIR) to determine functional groups present on the surface of unexposed and weathered WPCs [6]. By following carbonyl growth, we were able to conclude that both the pigment and UVA delayed the eventual increase in surface oxidation and decrease in HDPE crystallinity that would occur at later exposure times [6]. Following our approach, Muasher and Sain also used FTIR to evaluate carbonyl growth in photostabilized WPCs. They identified a correlation between carbonyl growth and photostabilizer effectiveness at reducing color fade [5].

Table 1 illustrates the percent change in property that occurs after injection molded, photostablized WPCs weather [7]. The results clearly showed that composites with an ultraviolet absorber (UVA) or pigment (P) lightened less than unstabilized composites. The pigment (P) was more efficient at preventing composite lightening than UVA. Lightness (L*) decreased with increase in pigment concentration. By contrast, increasing UVA content had little, if any, effect on L*. Composites with the least amount of lightening had a combination of UVA and P. It was concluded that UVA reduces lightening by absorbing some UV radiation, resulting in less UV

radiation available to bleach the wood component, while P physically blocks UV radiation, which also results in less available UV radiation to the wood component. In addition, P masks some lightening [7].

I	Table 1. Percent change in properties of 50% wood flour filled HDPE composites after 3000	
I	hours of accelerated weathering [7]	

	Change in Property (%)		
Formulations	L^*	Strength	MOE
	+ 115	- 27	- 33
0.5% UVA	+ 98	- 20	- 32
1% UVA	+ 107	- 15	- 21
1% P	+ 73	- 13	- 18
2% P	+ 61	- 5	- 18
0.5% UVA, 1% P	+ 59	- 9	-15
1% UVA, 2% P	+ 50	- 2 ^{NS}	- 16

UVA: Hydroxyphenylbenzotriazole, Tinuvin 328, Ciba Specialty Chemicals

P: Zinc ferrite in carrier wax, Cedar TI-8536, Holland Colors Americas

NS: Change not significant at $\alpha = 0.05$

Adding 0.5% UVA did not greatly influence the loss in MOE but did improve the loss in strength (Table 1). Increasing the UVA concentration to 1% resulted in further retention of MOE and strength. Adding P at 1% resulted in smaller MOE and strength losses than did adding 1% UVA. Increasing the concentration of P did not change the loss in MOE but decreased the loss in strength. Based on FTIR work, it was suggested that UVA and P delay changes in HDPE crystallinity [6]. UVA was likely consumed during weathering, therefore the higher concentration was required to protect against mechanical property loss for the full weathering period. The P consisted of zinc ferrite in a carrier wax. The wax may protect the WPC by creating a hydrophobic surface and resulting in less degradation of the interface [7].

Processing Conditions

Injection molding, compression molding, and extrusion are processing methods commonly used for manufacturing WPCs. Primary processing variables include temperature and pressure. Both processing methods and variables within a processing method greatly influence composite morphology and properties.

Injection molding composites results in a skin-core morphology. In polymeric composites made with short fibers, fibers in the core layer are oriented perpendicular to flow while those in the skin layer are oriented parallel to flow [21,22]. Processing variables can affect the relative

thickness of these layers. A low mold temperature can lead to a very thick skin [21]. Increasing barrel temperature, screw speed, and injection speed decreases skin thickness [21]. Not only does the morphology of injection molded composites change from the skin to the core, but the volume fraction of the fiber can change as well. For injection molded cellulose fiber filled polypropylene, fiber volume fraction was slightly higher in the core layer than the surface layer [22]. In addition, injection molded composites often have a polymer-rich surface layer [8,17].

The following example illustrates how different manufacturing methods affect WPC weatherability. We manufactured 50% WF filled HDPE composites using either injection molding or extrusion. Composite surfaces analyzed using FTIR spectroscopy and SEM microscopy. Composite lightness (L*), and flexural properties were also determined [8].

Before Weathering

The FTIR spectra of the extruded surface had larger peaks associated with wood (a broad peak at 3318 cm⁻¹ and a strong peak at 1023 cm⁻¹) compared with the injection molded surface. This suggested more wood at the surface of the extruded samples. SEM micrographs supported this. The surface of the injection molded sample was relatively smooth, and polymer flow over wood particles was evident. The surface of the extruded sample had many voids where the polymer failed to encapsulate the wood particles. Higher processing temperatures and pressures resulted in more plastic at the surface of injection molding composites compared with extruded composites [8].

After Weathering

SEM micrographs showed surface cracking of the polymer matrix after weathering. In addition, swelling and shrinking of the wood particles after absorbing and desorbing moisture resulted in voids at the wood flour/HDPE interface. Surface cracking and destruction of interfacial properties continued as weathering time increased, and the composite surface began to flake off. Extruded composites were more degraded after weathering than injection molded composites [8].

The effect of weathering on composite lightness, L*, is shown in Table 2. Unexposed surfaces of injection molded composites were the darker than extruded surfaces. Processing temperature was higher for injection molded samples, which resulted in a darker composite due

to some wood degradation. Weathering clearly resulted in lightening of the composite. The study showed that although the WPCs lightened to a similar L* after 3000 hours of weathering, after 1000 hours of weathering L* of extruded composites was closer to the final L* than for injection molded composites [8].

Table 2. Lightness	(L^*) of WF	filled HDPE	
composites after accelerated weathering.			
L*			
Weathering Time	Injection	Extruded	
(Hours)	Molded		
0	49	57	
1000	78	85	
2000	86	88	
3000	90	91	

Composite weathering resulted in a decrease in both flexural strength and MOE (Table 3). After both 1000 and 2000 hours of weathering, injection molded composites retained more strength than extruded composites. After weathering 3000 hours, strength retention of extruded and injection molded composites was similar. After all weathering periods, the retention of MOE was larger for the injection molded composites compared with the extruded composites [8].

These results led to the conclusion that processing variables have a large effect on WPC surfaces; generally higher temperatures and pressures result in more plastic at the surface. The composites exposed were to two

Table 3. Relative fle		ies of WF fill	ed HDPE con	nposites after
accelerated weathering	ccelerated weathering.			
Exposure Time	Strength		Time Strength MOE	
(Hours)	(MPa)		(GPa)	
	Injection	Extruded	Injection	Extruded
	Molded		Molded	
0	1	1	1	1
1000	0.88	0.77	0.81	0.60
2000	0.82	0.65	0.67	0.47
3000	0.68	0.66	0.57	0.48

weathering variables, light radiation and water spray, which act to degrade WPCs. The presence of the hydrophobic plastic-rich surface layer delayed changes that occurred during weathering by preventing some degradation due to water exposure [8].

Weathering Exposure

Primary weathering variables include radiation (solar, ultraviolet, xenon-arc, etc.), temperature, and water. Secondary variables include seasonal and annual variation, geographical differences, atmospheric gases, and pollution changes. Accelerated weathering is a technique used to compare performance by subjecting samples to cycles that are repeatable and reproducible. The primary weathering variables can all be measured during accelerated weathering. During xenon-arc accelerated weathering, test standards are typically followed that

prescribe a schedule of radiation (irradiance at a specific wavelength) and water spray (number and time of cycles).

UV light and moisture exposure are detrimental to WPCs. In the following example, extruded WPCs (50% wood flour filled HDPE) were subject to two accelerated weathering cycles. The composites were weathered for approximately 3000 hours, with a radiant energy exposure of around 122 kW-h/m². The first weathering cycle included water spray cycles (12 minutes of water spray every two hours); in the second weathering cycle there was no water spray. The change in composite properties is shown in Table 4 [9].

Exposure to each weathering cycle clearly resulted in composite lightening (Table 4). However, the increase in L* was much less when the samples were exposed to UV light only

Table 4. Percent change in extruded 50% wood flour filled HDPE				
composites after acce	composites after accelerated weathering [9].			
Property	Property Weathering Cycle			
	UV + Water Spray	UV Only		
Lightness (L*)	+ 46	+ 13		
MOE	- 52	- 12		
Strength	- 34	+ 1 ^{NS}		
NS: Change not significant at $\alpha = 0.05$				

demonstrating that water spray has a large effect on color fading [9].

The color of WPCs primarily reflects the color and color change of the wood during weathering. Water exposure may contribute to discoloration through physical mechanisms. Washing the degraded surface by water spray exposed new wood surfaces for further degradation and resulted in a cyclical erosion of the surface as the lignin is degraded and subsequently washed away, exposing more lignin to degradation [23]. Additionally, washing the surface can remove some of the extractives that impart color. We concluded that the removal of the main components that impart color, the extractives, was probably the main reason for the majority of color fade [9].

UV light and water may also act synergistically to degrade the WPCs in the following way. Exposing the WPC to UV light degraded hydrophobic lignin, leaving hydrophilic cellulose at the surface which increased the surface wettability, causing the surface to become more sensitive to moisture [24]. This can be detrimental for two reasons. The first is that the presence of water in wood accelerates oxidation reactions that are a direct result of photodegradation. The second reason is that wood cell walls swell when penetrated by water, facilitating light penetration into the wood providing sites for further degradation [12].

Flexural MOE and strength decreased when the composites were exposed to UV light with water spray (Table 4). Exposing the WPCs to UV light only resulted in a small decrease in MOE for the extruded composites and no significant change in strength. Exposure to UV radiation with water spray resulted in more destruction in mechanical properties than exposure to UV radiation only [9].

Moisture exposure adversely affects the mechanical properties WPCs [14,15,18]. Cracks formed in the HDPE matrix due to swelling of the wood fiber may contribute to the loss of composite MOE. The water spray also washed away the degraded surface layer. In this manner, the composite surface became increasingly vulnerable to further moisture penetration. The loss in strength was likely due to moisture penetration into the WPC, which degraded the wood–polymer interface. This decreases the stress transfer efficiency from matrix.

Increased wettability of the surface as a result of UV light exposure and surface erosion and the development of microcracks in the composite allowed for increased moisture penetration as weathering continued. Similar to the effects observed with L*, the water spray eroded the surface, making new composite surfaces available for water penetration and photodegradation.

Summary and Conclusions

Wood-plastic composites experience both changes in color and mechanical property loss after weathering. Three main variables that impact how WPCs perform during weathering are photostabilization, processing conditions, and weathering variables.

Pigments, ultraviolet absorbers, and hindered amine light stabilizers have been used to mitigate damage to WPCs during weathering. Pigments are useful to protect against both color fade and mechanical property losses. To a lesser extent, ultraviolet absorbers and hindered amine light stabilizers also protect against mechanical property losses. The usefulness of a photostabilizer depends largely on the type chosen and concentration the WPCs.

Manufacturing conditions, including manufacturing method and processing variables, have a large effect on WPC durability. The manufacturing condition influences the surface morphology and distribution of the WPC components. This has a direct influence on durability. Manufacturing WPCs with more plastic at the surface will result in delayed lightening and loss of mechanical properties during weathering. Secondary processing conditions such as embossing, brushing, or machining will also affect WPC durability.

Weathering variables also influence WPC durability. Photodegradation and degradation due to moisture exposure act in conjunction with one another. Exposure to light alone causes only small changes in composite properties. Preventing moisture exposure is a key element in improving WPC durability. Changing the manufacturing conditions is one effective technique that can prevent or delay degradation due to moisture exposure.

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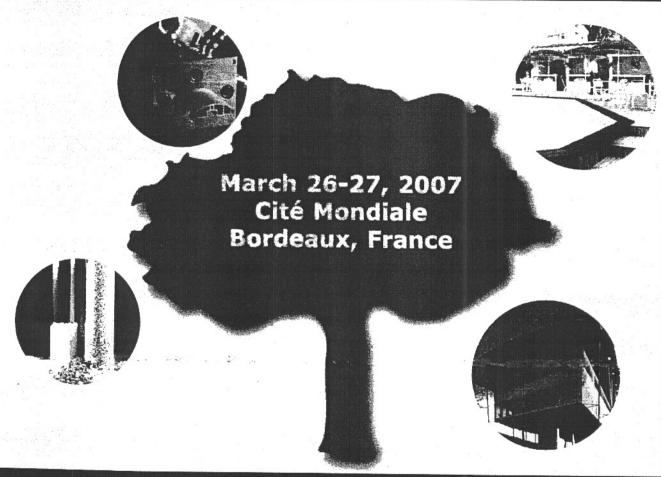
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